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The Mercury-Sensitized Reaction Between Hydrogen and Nitric Oxide

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The reaction of hydrogen atoms with nitric oxide has been studied by mercury sensitization of various mixtures of hydrogen and nitric oxide to produce nitrogen and water. The rate at constant nitric oxide pressure is proportional to the hydrogen at low hydrogen pressures, the effect diminishing at higher concentrations. With a given hydrogen concentration nitric oxide is almost without effect until an excess is present when it shows a retardation. At constant total pressure a maximum rate occurs with a particular excess of hydrogen. A mechanism based on HNO radicals has been postulated. These radicals decompose by a wall reaction to give nitrous oxide which is rapidly reduced to nitrogen.

THE homogeneous reaction between nitric oxide and hydrogen[1] is approximately third order, proceeding at measurable speed only above 700°C. The apparent activation energy of 49 kcal. coupled with a high rate constant makes it impossible to reconcile a termolecular mechanism similar to those for the reactions of nitric oxide with oxygen, chlorine, and bromine. The high rate constant alone would suggest a chain mechanism and the tests for such chains already applied[1b] are not unequivocal. From the complexity of the hydrogen-oxygen reaction taken in conjunction with the many similarities between nitric oxide and oxygen it would be surprising if the nitric oxide-hydrogen reaction was not relatively complex, probably involving hydrogen atoms originating either at a surface as in the hydrogen-oxygen reaction or in the gas phase by thermal dissociation of molecules as in the homogeneous para-ortho conversion. That hydrogen atoms will react with nitric oxide has been demonstrated by Harteck[2] who showed the production of a yellow deposit at liquid air temperature of the formula $(HNO)_n$ which decomposed at higher temperatures. It seemed advisable, therefore, to study more carefully the kinetics of the hydrogen atom reaction.

EXPERIMENTAL

Hydrogen atoms were produced by mercury sensitization. To this end a low pressure quartz-mercury arc, spiral in form and energized with a 0.265-kva transformer, was clamped alongside a cylindrical quartz reaction vessel connected to reservoirs of reactants, a manometer, and pump system. The reaction vessel and lamp were enclosed and temperature equilibrium at about 100°C was reached with the lamp operating before the reaction began. The lamp has an estimated yield of about 90 percent of its energy at 2537A.

[1] (*a*) C. N. Hinshelwood and T. E. Green, J. Chem. Soc., p. 730 (1926); (*b*) J. W. Mitchell and C. N. Hinshelwood, *ibid.*, p. 378 (1936).

[2] P. Harteck, Ber. 66, 423 (1933).

TABLE I. Pressure change in cm.

Time (min.)	Expt. 41 P_{H_2} = 7.65 P_{NO} = 10.0	Expt. 46 10.2 10.0	Expt. 50 10.05 5.4
2	0.45	0.8	0.85
4	1.4	1.9	1.9
6	2.35	3.0	2.9
8	3.35	4.1	3.75
10	4.3	5.1	4.45
12	5.25	6.1	5.05
14	6.05	7.1	5.5
16	6.85	7.95	5.85
18	7.6	8.75	6.05
20	8.3	9.55	6.25
25	9.75	11.3	6.65
30	10.55	12.6	7.05
35	10.8	13.55	7.4
40	10.95	13.95	7.65
50	11.15	14.25	7.8

Since water is one of the products of reaction and since it was simplest to follow the rate by pressure change, a large initial lag in pressure change until the vessel was saturated with water vapor was obviated by saturating the system initially with water. It was found that this did not affect the time needed for the completion of the reaction.

Nitric oxide was prepared from nitrosyl-sulfuric acid by treating its solution in sulfuric acid with mercury. Tank hydrogen was purified from oxygen by passage over hot platinized asbestos and was saturated with mercury vapor by bubbling through two traps containing mercury, the first one hot, the second at room temperature.

The products of some runs were analyzed by removal from the reaction vessel with a Toepler pump through a trap immersed in liquid nitrogen. The volume of the gases, nitrogen and hydrogen, thus withdrawn was measured. They were then burned over copper oxide at 325°C and the volume of the residual nitrogen determined. The liquid nitrogen around the trap was replaced with dry ice and the volume of gas released measured. Only in experiments with excess nitric oxide was any gas released. Hence this volume was taken to be residual nitric oxide indicating that no ammonia is formed during the reaction. The residual contents of the trap diluted with water always had a *p*H of seven, showing absence of basic and acidic nitrogen compounds.

TABLE II. Dependence of rate on hydrogen.

Expt.	P_{NO} (cm)	P_{H_2} (cm)	Rate (cm/min.)	k
42	9.9	3.7	0.28	1.61
45	10.15	4.65	0.34	1.67
41	10.0	7.65	0.48	1.70
46	10.0	10.2	0.54	1.63
44	10.4	10.6	0.58	1.68
40	10.2	20.3	0.76	1.70
43	10.3	21.1	0.75	1.66

RESULTS

In Table I are listed the actual pressure changes as a function of time for three typical experiments. A very brief initial induction period is succeeded by a fairly steady rate over many minutes. This maximum rate has been taken as the rate for the known initial partial pressures of the reactants.

Table II shows the variation of this rate with varying partial pressures of hydrogen at constant nitric oxide pressure. While the rate is approximately proportional to the hydrogen at low pressures, this effect is considerably diminished at high pressures. Thus the relative increase in rate between experiments 42 and 41, the latter at twice the hydrogen pressure of the former, is markedly greater than the relative increase in rate between runs 41 and 43 where the hydrogen ratio is almost three to one. The constant k in this and subsequent tables will be discussed later.

TABLE III. Dependence of rate on nitric oxide.

Expt.	P_{H_2} (cm)	P_{NO} (cm)	Rate (cm/min.)	k
50	10.05	5.4	0.51	1.49
52	11.6	8.05	0.51	1.40
46	10.2	10.0	0.54	1.63
47	10.15	20.95	0.28	1.11
51	10.05	24.4	0.27	1.17

The dependence of the rate on nitric oxide at constant hydrogen pressure is shown in Table III. It will be seen that there is little change in rate until nitric oxide and hydrogen are present in equal amounts but that an excess of nitric oxide has a retarding effect.

Since from the above it appears that the total pressure as well as the partial pressures of the reactants has an effect on the rate, a series of runs was made at constant total pressure with varying proportions of hydrogen and nitric oxide. The data are presented in Table IV.

Inspection of these data shows a maximum in the rate where the ratio of hydrogen to nitric oxide is slightly greater than two to one. This means that, for this particular total pressure, the rate is empirically dependent on a power of the hydrogen pressure and a power of the nitric oxide pressure which is a little less than one-half that of the hydrogen pressure.

Several runs not included in the above tables are given in Table V; their significance will appear in the discussion later.

The results of the gas analysis of the final products from three runs on completion of the runs are given in Table VI. The calculated results are on the basis of complete reduction of one mole of nitric oxide by one mole of hydrogen to produce nitrogen and water.

Experiments performed to test the effect of the radiation on mercury-saturated moist nitric oxide in the absence of hydrogen, showed that a reaction occurred slowly whose products contained brown nitrogen tetroxide and nitrogen. The former was never observed in the presence of excess hydrogen and is probably negligible. However, such a reaction could account for the small amount of residual nitric oxide and the excess of nitrogen observed in the above analysis of the mixture containing excess nitric oxide. The slowness of this reaction, however, should not affect the interpretation of the observed maximum rate of pressure change as the rate of the reaction producing nitrogen and water. Finally, in the other two runs in Table VI the fact that the hydrogen observed exceeds the calculated may be attributed to the order in which the gases entered the reaction vessel, hydrogen being always the last, leaving the possibility of some hydrogen in the capillary connecting tubes which never entered into the reaction vessel or perhaps that the rapidity of reaction made uncertain the initial hydrogen pressure reading which may thus be slightly low.

TABLE IV. Dependence of rate on composition at constant total pressure.

Expt.	P_{H_2} (cm)	P_{NO} (cm)	Rate (cm/min.)	k
63	14.65	1.25	0.20	1.01
58	12.55	2.45	0.35	1.21
61	11.85	3.20	0.40	1.25
62	9.90	5.00	0.41	1.21
60	9.80	5.45	0.41	1.21
59	8.50	6.65	0.41	1.28
68	7.50	7.45	0.36	1.21
66	6.95	7.95	0.36	1.27
69	6.35	8.90	0.31	1.19
67	3.70	11.35	0.20	1.22
64	2.15	13.15	0.10	1.04
65	1.25	13.45	0.06	1.03

TABLE V.

Expt.	P_{H_2} (cm)	P_{NO} (cm)	Rate (cm/min.)	k
48	13.10	5.25	0.56	1.50
49	12.50	5.25	0.53	1.44
53	5.95	5.30	0.41	1.50
54	5.10	5.15	0.41	1.62
55	10.30	4.85	0.45	1.33
56	16.95	5.85	0.54	1.32
57	23.25	5.55	0.53	1.21
71	7.10	9.70	0.32	1.17
72	8.40	16.05	0.29	1.15
73	27.75	8.05	0.53	1.09
74	5.55	3.40	0.31	1.20
75	10.15	9.00	0.37	1.10
76[a]	7.90	8.50	0.41	1.37
77	9.30	7.85	0.43	1.31
78	10.30	7.05	0.46	1.32
79	6.90	6.40	0.33	1.14
81	10.05	8.35	0.38	1.12
87[b]	11.95	11.55	0.59	1.70

[a] Reaction vessel cleaned on outside and flamed while evacuated.
[b] Reaction vessel cleaned inside and out.

DISCUSSION

The following mechanism is suggested to account for the above observations:

$$Hg + h\nu \rightarrow Hg^*; \quad (1)$$

$$Hg^* + H_2 \rightarrow Hg + 2H; \quad (2)$$

$$Hg^* + NO \rightarrow Hg + NO; \quad (3)$$

$$H + NO \rightarrow HNO; \quad (4)$$

$$H + HNO \rightarrow H_2 + NO; \quad (5)$$

$$HNO \rightarrow \text{decomp.} \quad (6)$$

Reactions (1) and (2) constitute the well-known mercury sensitized dissociation of hydrogen.

TABLE VI.

	P_{H_2} 10.30 obs.	P_{NO} 7.05 calc.	P_{H_2} 6.55 obs.	P_{NO} 7.45 calc.	P_{H_2} 11.95 obs.	P_{NO} 11.55 calc.
N_2 cc	7.30	7.35	8.2	6.8	11.6	11.9
H_2 cc	7.00	6.70	—	—	1.6	0.8
NO cc	—	—	0.05	1.85	—	—

TABLE VII. Reaction of nitrous oxide and hydrogen.

Expt.	P_{H_2} (cm)	P_{N_2O} (cm)	Rate (cm/min.)
91	10	4.95	0.30
92	10	1.60	0.20

Reaction (3) is in accord with the very efficient quenching of mercury fluorescence by nitric oxide observed by Bates[3] and also by Noyes[4] who shows that practically no chemical change ensues from such quenching.

Reaction (4) follows from the findings of Harteck[2] in experiments at low temperature. The association of a two-body collision is analogous to the two-body formation of HO_2 from H and O_2 based on the similarity of O_2 and NO. The possibility of the formation to any appreciable extent of OH and N, or of NH and O in reaction of H and NO is ruled out by the fact that no ammonia could be discovered among the products. This would also validate current estimates of the bond strengths of OH and NH in comparison with that of NO.

Harteck's observation of a stable compound $(HNO)_n$ at liquid air temperatures, identified by him as similar to the intermediate obtained in ammonia oxidation and which decomposed at $-95°C$ into nitrous oxide and water, suggests that the compound was probably nitramide or its isomer hyponitrous acid. Smallwood[5] has shown that nitric oxide catalyzes the recombination of hydrogen atoms produced in a discharge tube. He states that over 99 percent of the nitric oxide was recovered unchanged and suggests reactions (4) and (5) to account for the observation. Work in this laboratory by Dr. O. C. Wetmore has also shown that no nitrogen is produced when nitric oxide is allowed to react with hydrogen atoms drawn from a discharge tube. That considerable amounts of nitrogen and water are found in the photosensitized system can only be attributed to the difference in the experimental conditions. In the latter, the system is static and hydrogen atoms are being continuously formed. In the discharge-tube reactions, the system is dynamic. If only a small fraction of the HNO produced decomposed into nitrous oxide and water and most of it reacted with hydrogen atoms, the decomposition could be negligible in the flow system but cumulative in the static system.

A possible mechanism for the decomposition of HNO may be the following:

$$2HNO \rightarrow (HNO)_2; \quad (6a)$$

$$(HNO)_2 \rightarrow N_2O + H_2O; \quad (6b)$$

$$N_2O + H \rightarrow N_2 + OH; \quad (6c)$$

$$OH + H_2 \rightarrow H_2O + H. \quad (6d)$$

Although these reactions may be considered as speculative they are not without foundation. Melville[6] gives the energy of activation of reaction (6c) as 15–20 kcal. If this were so the reaction would be relatively slow. Taylor and Marshall,[7] however, found that the mercury sensitized reaction between hydrogen and nitrous oxide proceeds much more rapidly than that between hydrogen and oxygen. It appears that nitrous oxide should be reduced as fast as it is formed. To test this the rate of reaction between nitrous oxide and hydrogen was measured under conditions exactly similar to those previously. The results of two runs are presented in Table VII. An average rate for the nitric oxide reaction at a hydrogen pressure of 10 cm is 0.45 cm/min. From the over-all reaction

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O,$$

such a rate of pressure change corresponds to 0.30 cm/min. of nitric oxide reacting, or, from the above mechanism to the formation of 0.15 cm/min. of nitrous oxide. Now the over-all nitrous oxide reaction is

$$N_2O + H_2 \rightarrow N_2 + H_2O,$$

whence the observed rate of pressure change is equal to the rate of disappearance of nitrous oxide. The observed rate of disappearance of nitrous oxide even at 1.60 cm is thus faster than its rate of production in the nitric oxide reaction, indicating that it cannot accumulate in the system. The hydrogen atoms required for reac- (6c) balance those produced in (6d) and conse-

[3] J. R. Bates, J. Am. Chem. Soc. **54**, 569 (1932).
[4] W. A. Noyes, Jr., J. Am. Chem. Soc. **53**, 514 (1931).
[5] H. M. Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929).
[6] H. W. Melville, Proc. Roy. Soc. **A146**, 737 (1934).
[7] H. S. Taylor and A. L. Marshall, J. Phys. Chem. **29**, 1140 (1925).

quently there is no disturbance of the stationary atom concentration in the system. Even if the above mechanism is incorrect the fact remains that nitrous oxide cannot accumulate in the system and unless the actual mechanism involves hydrogen atoms or HNO radicals in such a way as to disturb the stationary concentrations of these as calculated later the mechanism of nitrous oxide reduction is not relevant here.

The over-all decomposition of HNO is expressed in reaction (6) as a first-order reaction since the subsequent analysis will show this is in agreement with the observed data whereas a second-order rate is not. The first-order rate suggests that the reaction occurs on the surface.

From reactions (1), (2), and (3) the stationary concentration of excited mercury atoms is given by

$$P_{Hg}^* = I/(k_2 P_{H_2} + k_3 P_{NO}),$$

where I is the intensity of the light absorbed. The stationary concentration of hydrogen atoms given by reactions (2), (4), and (5) after eliminating HNO by reactions (4), (5), and (6) must be obtained from a quadratic equation in P_H. Comparison of various approximate solutions of this equation with the experimental results shows that the simplest and soundest approximation will be of the form

$$P_H = (AP_{NO} + B)/P_{NO},$$

where A and B are taken as constants, whereas B would actually be the difference of two approximately equal terms involving P_{Hg}^*, P_{H_2}, or P_{NO}. With this value of P_H, the over-all rate of disappearance of nitric oxide as measured by $k_6 P_{HNO}$ is found to be:

$$-dP_{NO}/dt = k_6 P_{HNO} = k_6 \frac{2k_2 P_{Hg}^* P_{H_2}}{2k_5 P_H + k_6}$$

$$= \frac{2k_2 k_6 P_{Hg}^* P_{H_2} P_{NO}}{(2k_5 A + k_6) P_{NO} + 2k_5 B}$$

$$= \frac{kP_{H_2} P_{NO}}{\left(P_{H_2} + \frac{k_3}{k_2} P_{NO}\right)(P_{NO} + K)},$$

where

$$k = 2k_6 I/(2k_5 A + k_6)$$

TABLE VIII.

Time (min.)	Expt. 41 k	Expt. 46 k	Expt. 50 k
2	0.51	0.78	0.81
4	1.10	1.10	1.05
6	1.14	1.13	1.06
8	1.25	1.17	0.96
10	1.25	1.10	0.86
12	1.33	1.25	0.80
14	1.20	1.21	0.66
16	1.29	1.08	0.56
18	1.32	1.08	0.35
20	1.37	1.15	0.36
25	1.44	1.16	0.32
30	1.22	1.13	0.40
35	0.55	1.16	0.46
40	0.42	0.69	0.46
50	0.63	0.34	0.20

and

$$K = 2k_5 B/(2k_5 A + k_6).$$

According to Bates[8] the number of effective collisions per second at unit pressure between activated mercury atoms and nitric oxide molecules is 1.25×10^{-7} while for hydrogen the value is 1.13×10^{-7}. Hence $k_3/k_2 = 1.1$.

Experiments at a total pressure of 15 cm (Table IV) show that at this pressure the rate of reaction is a maximum when the ratio of hydrogen to nitric oxide is slightly greater than two. This condition is satisfied in the above rate equation when $K = 4.5$. Hence

$$\text{rate} = k \frac{P_{H_2} P_{NO}}{(P_{H_2} + 1.1 P_{NO})(P_{NO} + 4.5)}.$$

A value for k according to this equation has been calculated for each experiment and is listed in the previous tables. The rate used in the calculation is the maximum rate of pressure change and this has been taken as the rate for the initial pressures. This tends to give high values for k on account of the induction period since when the maximum rate is actually attained, some reaction has already occurred. Since the induction effect is approximately constant, these values of k, though high, may be used for comparative purposes. That the rate expression does give constant values for k throughout a given run is nevertheless shown in Table VIII where the k values corresponding to the pressure

[8] J. R. Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).

data in Table I are listed. In order to eliminate the effect of the induction period the rate equation was integrated from point to point during a run giving:

$$k(t_2-t_1)=2(x_2-x_1)$$
$$+(b-a+4.5)\ln\frac{a-x_1}{a-x_2}+4.5\ln\frac{b-x_1}{b-x_2},$$

where a and b are the initial pressures of hydrogen and nitric oxide, respectively, and x, measured by $\frac{2}{3}$ pressure change, is the amount decomposed in time t. The constancy is excellent save when hydrogen is in excess. This is to be attributed, not to any difference in the chemical behavior when hydrogen is in excess, but merely to the approximation which has been used in determining the stationary hydrogen atom concentration and naturally as the reaction progresses the effective excess of hydrogen increases and the approximation becomes worse as shown by the falling trend in experiment 50. The maximum value of the constant is nevertheless significant.

Inspection of the k values in Tables II, III, and IV shows good constancy in each set. In Table II the average deviation from the mean is well within experimental error. In Table III there is greater deviation. However, for slow rates the experimental accuracy is less, being for a rate of 1 mm per min. only about 25 percent. In Experiments 47 and 51 the low k value may be due to the presence of excess nitric oxide involving its reaction with water.

The variation of the constant from one set to another may appear significant. When all the experiments are grouped together in the order in which they were performed it is seen that the variation is a gradual decrease down to experiment 75. The variation cannot be attributed to differences in pressure or in the proportions of the reactants since individual experiments which were performed within one set are frequently repeated within another set and the k value found is in agreement with the average for the set. It must be concluded that the variation is due to a decrease in the illumination in the reaction vessel because of a mercury deposit on the inside and dust accumulation outside. The vessel and lamp were enclosed until after run 75. Inspection showed this condition to be true. When the outside of the reaction vessel was cleaned and flamed (see Table V) the value of k rose from 1.10 to 1.37. After the vessel had been cleaned thoroughly inside and out, run 87 showed a k value of 1.70 in agreement with the high values found in the earliest runs.

The apparent variation in the k values is thus mechanical, reflecting a variation in I_{abs} and it must be concluded that the suggested mechanism will account for the observations made.

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Raman Spectra of Hydrocarbons

IV. 2,5-Dimethyl-1,5-Hexadiene and 2,5-Dimethyl-2,4-Hexadiene[1]

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Raman frequencies, relative intensities, and depolarization factors are given for (A) 2,5-dimethyl-1,5-hexadiene and (B) 2,5-dimethyl-2,4-hexadiene. The relative intensities and depolarization factors were obtained with the aid of a Gaertner microdensitometer. The two molecules are isomers, each containing eight carbon and fourteen hydrogen atoms. (A) contains two $XYC=CH_2$ groups and (B) contains two $XXC=CHZ$ groups. In (B) the double bonds are conjugated, in (A) unconjugated. The results for the five olefinic frequencies are compared with data previously obtained for nine other olefins. The data for the olefinic lines of (A) are 1297(50), 1414(430)0.74, 1651(1000)0.21, 2977(580)0.28, and 3074(220)0.78, values which are in good agreement with those obtained previously for olefins containing an $XYC=CH_2$ group. For (B) the olefinic frequencies are 1227(75)0.46, 1663(1000)0.18, 3012(vw), and 3040(vw) (vw = very weak). The conjugation thus resulted in a lowering of these frequencies of 19, 19, 0, and 10 cm^{-1}, respectively, from the values of the corresponding frequencies of the $XYC=CHZ$ group in dipentene.

INTRODUCTION

DIOLEFINS which contain conjugated double bonds yield a lower value for the olefinic frequency near 1600 cm^{-1} than do olefins having unconjugated double bonds. The two olefins, 2,5-dimethyl-1,5-hexadiene and 2,5-dimethyl-2,4-hexadiene, concerned in the present study represent examples of these two classes of unsaturated hydrocarbons. Previous papers of this series[2] have reported results obtained in experimental investigations of two olefins containing an $XHC=CH_2$ group, three containing an $XYC=CH_2$ group, three containing an $XHC=CHY$ (*trans*) group, one containing an $XHC=CHX$ (*cis*) group, and one containing an $XYZ=CHZ$ group. Tabulation and comparison of the results for these olefins indicated that the set of five olefinic frequencies have characteristic differences for the different groups. Only one of the olefins, dipentene, was a diolefin, and it was a ring compound with one of the double bonds in the ring and one outside the ring.

The present investigation extends the above work to include two isomeric diolefins with open chains, one having conjugated double bonds, the other having unconjugated double bonds. No previous Raman spectra data seem to have been reported for these compounds.

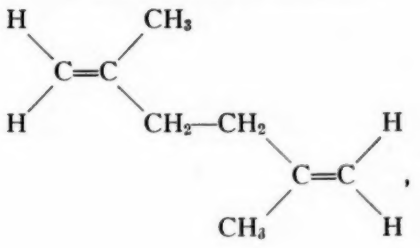
EXPERIMENTAL

The apparatus and experimental technique were described in the first two papers[2] of this series. The spectrograms were made with the samples in the liquid state and excitation was by Hg 4358A.

In order to inhibit peroxide formation, the samples were shipped to this laboratory in the presence of hydroquinone. The sample, with the small amount of hydroquinone, was placed into the flask, attached to the Raman tube through a side tube sealed into the flask, and the hexadiene was distilled over into the Raman tube in an atmosphere of nitrogen by heating slowly, with constant shaking, in an oil bath.

The methods of preparation and the physical properties of the compounds were as follows:

2,5-Dimethyl-1,5-hexadiene



[1] Presented at the American Physical Society meeting, Evanston, Illinois, November 13, 1943.
[2] Forrest F. Cleveland, J. Chem. Phys. **11**, 1, 227, 301 (1943).

C_8H_{14}: prepared by condensation of methallyl chloride on magnesium in ethyl ether; purified by fractional distillation; chemical tests for halogens and peroxides, negative; f. p. −75.6°C; b. p. 114.3°C; n_D^{20}, 1.4293, d_4^{20}, 0.74230.

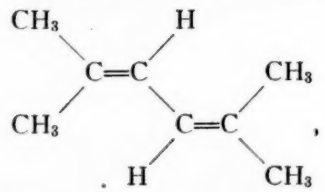
TABLE I. Raman spectra of the two diolefins.*

2,5-Dimethyl-1,5-hexadiene			2,5-Dimethyl-2,4-hexadiene		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
222	37				
252	66				
281	40		279	13	
			295	28	0.14
318	42				
			343	14	
365	85				
395	87		396	vw	
416	110	0.76			
438	27		437	vw	
			469	26	0.88
495	59		506	13	
528	82	0.32			
690	41	0.35			
764	97	0.17			
			836	22	0.65
851	92	0.08			
			860	16	0.90
888	140	0.87			
960	20	*D*			
1014	62	0.39	1032	vw	
1057	61	0.41	1070	12	*D*
1162	24		1157	210	0.42
1210	29	0.44	1227	75	0.46
1258	23				
1297	50				
1334	41				
			1366	87 }	0.29
1380	150	0.61	1383	160 }	
1414	430	0.74			
1431	190	0.78	1446	70	0.52
1651	1000	0.21	1663	1000	0.18
			**1719	8	
2724	28	*P*	2733	5	
2844	230	*P*			
2864	290	*P*	2867	60	*P*
2900	960	0.18			
			2914	180	0.19
2926	450	0.51			
			2964	25	*D*
2977	580	0.28	2991	21	*P*
			3012	vw	
			3040	vw	
3074	220	0.78			

* $\Delta\nu$ is the Raman frequency in cm^{-1}, I is the relative intensity based upon a value of 1000 for the strongest Raman line on the plate, ρ is the depolarization factor, vw (very weak) designates lines that were too weak to measure with the microdensitometer, *P* and *D* indicate polarized and depolarized lines, respectively, for which the weaker component of the polarization doublet was too weak to measure with the microdensitometer, and the brace encloses lines that were not resolved on the polarization spectrogram.

** This line is probably due to an impurity containing C=O.

2,5-Dimethyl-2,4-hexadiene



C_8H_{14}: prepared by rearrangement of 2,5-dimethyl-1,5-hexadiene over alumina at 380°C; purified by rapid distillation, followed by fractional crystallization; chemical tests for halogens and peroxides, negative; f. p. 13.9°C; b. p. 134.5°C; n_D^{20}, 1.4781; d_4^{20}, 0.7615.

RESULTS

The Raman data obtained for the two hexadienes are listed in Table I. The accuracy of the relative intensities was discussed in the second paper of the series.[2] To avoid giving the impression that the relative intensities are too accurately known, only two significant figures are retained.

DISCUSSION

The spectra of the two isomeric hexadienes are remarkably different from each other, only the five lines near 280, 395, 438, 1380, and 2864 cm^{-1} having—within experimental error—the same frequencies in the two spectra.

Since the chief interest in this series of investigations is the variation in the olefinic frequencies when the double bond occupies different positions in various molecules, it seems desirable to list again in tabular form the olefinic frequencies previously obtained, together with the olefinic frequencies of the present two hexadienes, in order to facilitate the comparison of these frequencies for the various groups in the various compounds. This is done in Table II. One might think from a casual inspection of the data in Table I that conjugation increases the frequency near 1650 cm^{-1}. This would be incorrect, however, since the olefinic group is not the same in the two hexadienes. It is more significant to compare the frequencies for the XYC=CHZ group in dipentene with those of the XXC=CHZ group in 2,5-dimethyl-2,4-hexadiene; the 1682-cm^{-1} frequency in dipentene appears at 1663 cm^{-1} in the spectrum of 2,5-dimethyl-2,4-hexadiene. Hence the effect of the conjugation—as is well

TABLE II. Comparison of the olefinic frequencies for the various groups.

							$H_2C=CH_2$								
Ethylene*	1341	St**	0.17				1619	St	P	3009	St	0.10	3075	—	—
							$XHC=CH_2$								
1-Octene	1293	94	0.88	1415	42	0.77	1641	130	0.15	2999	120	0.28	3078	23	0.93
6-Methyl-1-heptene	1295	210	0.45	1417	110	0.56	1644 1672	340 vw	0.19	3001	230	0.27	3079	70	0.73
							$XYC=CH_2$								
2-Methyl-1-heptene	1303	52	0.64	1414	110	0.81	1653 1674	200 55	0.20 *P*	2978	250	*P*	3077	47	0.70
2,4,4-Trimethyl-1-pentene	1295	vw		1410	150	0.62	1644 (1658	160 51	0.33 *P*)	2977	790	*P*	3072	32	0.71
Dipentene	1290 1311	46 54	0.72 0.73	1376	130	0.70	1648	210	0.38	2983	110	*P*	3078	16	*D*
2,5-Dimethyl-1,5-hexadiene	1297	50		1414	430	0.74	1651	1000	0.21	2977	580	0.28	3074	220	0.78
							XHC=CHY (*trans*)								
2-Octene	1300	40	0.64	—	—	—	1672	47	0.23	3004	37	0.34	—	—	—
3-Octene	1303	87	0.56	—	—	—	1672	170	0.16	2998	59	0.29	—	—	—
4-Octene	1290	41	0.54	—	—	—	1672	150	0.19	2997	27	0.36	—	—	—
							XHC=CHX (*cis*)								
Cyclohexene	1241	81	0.64	—	—	—	1653	450	0.14	3023	510	0.19	3059	19	*D*
							XYC=CHZ								
Dipentene	1246	26	*D*	—	—	—	1682	220	0.35	3012	54	*P*	3050	26	*D*
							XXC=CHZ (conjugated)								
2,5-Dimethyl-2,4-hexadiene	1227	75	0.46	—	—	—	1663	1000	0.18	3012	vw		3040	vw	

* Data from M. Magat, *Tables Annuelles de Constantes et Données Numériques, Effet Raman* (Hermann et Cie, Paris, 1937), Vol. 12, p. 53.
** St = strong.

known from results with other molecules—is to *lower* the double bond frequency, in this case by 19 cm^{-1}. The conjugation also appears to lower the 1246- and 3050-cm^{-1} frequencies by 19 and 10 cm^{-1}, respectively, but not the one at 3012 cm^{-1}. One must be cautious in making this comparison, however, since for dipentene a ring structure is involved, while for the 2,5-dimethyl-2,4-hexadiene the structure is an open chain.

Examination of Table II shows that, if a single olefin were present in a mixture of saturated hydrocarbons, one could easily tell from the Raman spectra whether the group present was $XHC=CH_2$, $XYC=CH_2$, or $XHC=CHY$ (*trans*). The data on the other groups is as yet too meager to draw definite conclusions, but the indication is that one might also be able to recognize them by the characteristic values of the olefinic frequencies in their Raman spectra.

It is interesting to note that the 2,5-dimethyl-2,4-hexadiene, which contains no CH_2 groups, has quite different C—H frequencies in the 1350–1450-cm^{-1} and 2700–2965-cm^{-1} regions from those of the 2,5-dimethyl-1,5-hexadiene, which contains both CH_3 and CH_2 groups.

The weak line at 1719 cm^{-1} in the spectrum of the 2,5-dimethyl-2,4-hexadiene is probably due to a trace of some impurity containing a C=O group.

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The Electrostatic Contribution to Hindered Rotation in Certain Ions and Dipolar Ions in Solution. III

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In the present paper we shall extend the previous methods to a relatively complicated molecule, glutamic acid:

COOH (1)
|
$CHNH_3^+$ (3)
|
$(CH_2)_2$
|
COOH (2).

Other calculations will also be made and an empirical relationship among the effective dielectric constants found in this and earlier papers will be pointed out.

I. GLUTAMIC ACID

THE dissociation constants of glutamic acid and its esters have been measured quite accurately.[1] Assuming that a $-COOC_2H_5$ group and a $-COOH$ group have the same influence on the dissociation of a proton elsewhere in the molecule,[2] one can calculate[3] the twelve microscopic equilibrium constants relating the eight different microscopic ions of glutamic acid. These ions and dissociation constants are shown in Fig. 1. The notation is that used before.[3-6] The

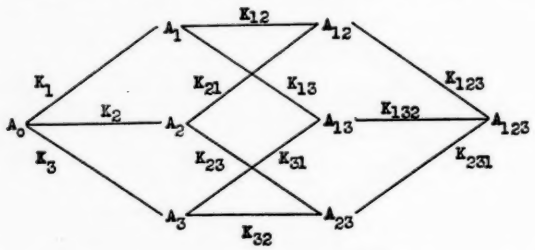

FIG. 1. Microscopic ions and dissociation constants of glutamic acid.

	pK		pK
1	2.148	23	7.838
2	3.846	31	4.303
3	7.035	32	4.649
12	4.315	123	9.960
13	9.190	132	5.085
21	2.617	231	4.739

[1] A. Neuberger, Biochem. J. **30**, 2085 (1936).
[2] E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids, and Peptides as Ions and Dipolar Ions* (Reinhold Publishing Corporation, New York, 1943), Chapter 4.
[3] T. L. Hill, J. Phys. Chem. (in press).
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[5] T. L. Hill, J. Chem. Phys. **11**, 552 (1943).
[6] T. L. Hill, J. Am. Chem. Soc. **65**, 2119 (1943).

$\alpha-COOH$, $\gamma-COOH$, and $-NH_3^+$ groups are numbered 1, 2, and 3, respectively.

Of the eight microscopic ions, four possess two or three charges within the molecular structure and therefore exhibit electrostatic hindered rotation. These ions are A_1, A_2, A_{123}, and A_{12}. Of the twelve microscopic equilibria, nine involve at least one of the four ions mentioned. The remaining three equilibria (with equilibrium constants K_{31}, K_{32}, and K_3) are used for reference, inasmuch as the dissociation of a proton in these cases does not involve any electrostatic "perturbation." That is, in our previous notation,

$$\begin{aligned} K_1^0 &= K_{21}^0 = K_{231}^0 = K_{31} \\ K_2^0 &= K_{12}^0 = K_{132}^0 = K_{32} \\ K_{13}^0 &= K_{23}^0 = K_{123}^0 = K_3. \end{aligned} \tag{1}$$

We are interested in the nine ratios K_1/K_1^0, $\cdots$, K_{123}/K_{123}^0. Because of the relationships between the microscopic dissociation constants,[3,6] only six of the nine ratios are independent. The six independent values of $\Delta pK = pK^0 - pK$ are given in Table I. Column (2) indicates the type of charge effect. Thus, $\Delta pK_1 = 2.155$ may be thought of as arising from a positive charge in the α-position with respect to the dissociating proton. The values in the third column are calculated by addition or subtraction from the individual α, γ, and δ effects in column (1). The observed ΔpK's are smaller in magnitude than the additive ΔpK's by 0.033 pK units.

If we let U, as before, represent the electrostatic potential energy of a microscopic ion, $U=0$ for A_0, A_3, A_{13}, and A_{23}. We proceed now to obtain approximate expressions for U_1, U_2, U_{123}, and U_{12}. We take the C–C distance as 1.54A, C–O as 1.25A, C–N as 1.41A, the O–C–C angle as 118°, N–C–C as 112°, and C–C–C as tetrahedral.

Clearly U_1, aside from the effective dielectric constant D_E, will differ only slightly from U for the dipolar ions of the α-amino acids previously discussed[4] (the C–C distances differ by 0.01A). U_1 in Tables II and III may be compared with the corresponding function in Table I.[4] The configurational angle θ'' is used here instead of θ.

In order to avoid undue complications in writing approximate functions for U_2 and U_{123}, we shall take the negative charge on a carboxylate group as residing midway between the two oxygen atoms. Then U_{123} may be written as a function of the two angles θ and θ' exactly as was done for 1,3-propane diamine.[5] The C-*negative charge* distance is 2.13A. We take θ as the angle of rotation of the negative charge at position 1 (α) and θ' as the angle of rotation at position 2 (γ).[5] The functions U_{123} and U_2 are included in Tables II and III, computed from the intercharge distances

$$r_{123}^2 = a_1 + a_2\cos\theta + a_3\cos\theta' + a_4\cos\theta\cos\theta' + a_5\sin\theta\sin\theta' \quad (2)$$

and

$$r_2^2 = a_1 + a_2\cos\left(\theta+\frac{2\pi}{3}\right) + a_3\cos\theta' + a_4\cos\left(\theta+\frac{2\pi}{3}\right)\cos\theta' + a_5\sin\left(\theta+\frac{2\pi}{3}\right)\sin\theta',$$

the negative charge at position 1 and the positive charge on the nitrogen atom being approximately 120° out of phase.

TABLE I.

	(1) $\Delta pK = pK^0 - pK$	(2) Charge effects	(3) ΔpK Additive	(4) D_E
K_1, K_1^0 (K_{13}, K_{13}^0)[a]	2.155	$+\alpha$		36.3
K_2, K_2^0 (K_{23}, K_{23}^0)[a]	0.803	$+\gamma$		82.6
K_{132}, K_{132}^0 (K_{231}, K_{231}^0)	−0.436	$-\delta$		129.
K_{12}, K_{12}^0	0.334	$+\gamma, -\delta$	0.367	(50.7)
K_{21}, K_{21}^0	1.686	$+\alpha, -\delta$	1.719	(16.8)
K_{123}, K_{123}^0	−2.925	$-\alpha, -\gamma$	−2.958	(50.6)

[a] The sign of ΔpK is negative.

TABLE II.

$U_0 = U_3 = U_{13} = U_{23} = 0$

$U_1/RT = A + C\cos 2\theta''$

$U_{123}/RT = A + B\cos\theta' + (C + D\cos\theta')\cos(\theta - \alpha\sin\theta')$

$U_2/RT = A + B\cos\theta' + (C + D\cos\theta')\cos\left(\theta + \frac{2\pi}{3} - \alpha\sin\theta'\right)$

$U_{12}/RT = (U_1 + U_{123} + U_2)/RT$

$V_{\text{all ions}} = \text{const.} + \frac{1}{2}V_0(\cos 3\theta + \cos 3\theta') + \frac{1}{2}V_0''\cos 6\theta''$

TABLE III.

	a_1	a_2	a_3	a_4	a_5	A	B	C	D
A_1						−0.3214		−0.0052	
A_{123}	21.56	−8.53	−8.53	−2.69	−8.06	.3291	0.1441	.1441	0.1260
A_2	18.19	−5.54	−7.83	−1.75	−5.25	− .3010	−.1034	− .0904	−.0760

a's in units of A^2; A, B, C, and D in units of A^{-1}.

U_{12} is written as the sum of U_1, U_{123}, and U_2. The approximate form of the non-electrostatic[4] restricting potential V is also given in Table II; V_0 and V_0'' are probably in the neighborhood of 3400 and 1000 cal./mole, respectively, the order of magnitude being the only point of importance here.

For any particular microscopic equilibrium, say

$$A_a \rightleftarrows A_i + H^+,$$

the microscopic equilibrium constant K is related to the corresponding unperturbed equilibrium constant K^0 by [Eq. (6)[4]]

$$K = K^0 \frac{\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \exp\{-[U^i(\theta,\theta',\theta'') + V(\theta,\theta',\theta'')]/RT\}\,d\theta d\theta' d\theta''}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \exp\{-[U^a(\theta,\theta',\theta'') + V(\theta,\theta',\theta'')]/RT\}\,d\theta d\theta' d\theta''}. \quad (3)$$

The integrations called for are again straightforward, using expansions in Bessel functions, but become quite laborious. Keeping in mind that these integrations are done on potential

functions which necessarily become more approximate the more complex the molecule, it would seem that a more satisfactory procedure, though still approximate, would be merely to sum over those configurations corresponding to minima in V (since V_0 is generally of the order of several kcal./mole). This method is simpler and at least as accurate, especially in complicated cases.

Since the summation method will be largely employed here, details of the integrations will be omitted and only the results stated [to about the same degree of accuracy as Eq. (12)[5]]:

$$\int\int\int e^{-V/RT}d\theta d\theta' d\theta'' = 8\pi^3 I_0^2\left(\frac{v}{2}\right) I_0\left(\frac{v''}{2}\right); \tag{4}$$

$$\int\int\int \exp\left[-(U_1+V)/RT\right]d\theta d\theta' d\theta'' = 8\pi^3 \exp\left(-A_1\right) I_0^2\left(\frac{v}{2}\right) I_0\left(\frac{v''}{2}\right) I_0(C_1); \tag{5}$$

$$\int\int\int \exp\left[-(U_{123}+V)/RT\right]d\theta d\theta' d\theta'' = 8\pi^3 \exp\left(-A_{123}\right) I_0\left(\frac{v}{2}\right) I_0\left(\frac{v''}{2}\right) \times (D_{0123}E_{0123}+\cdots+D_{3123}E_{3123}); \tag{6}$$

$$\int\int\int \exp\left[-(U_2+V)/RT\right]d\theta d\theta' d\theta'' = 8\pi^3 \exp\left(-A_2\right) I_0\left(\frac{v}{2}\right) I_0\left(\frac{v''}{2}\right) \times (D_{02}E_{02}+\cdots+D_{32}E_{32}); \tag{7}$$

$$\int\int\int \exp\left[-(U_{12}+V)/RT\right]d\theta d\theta' d\theta'' = 8\pi^3 \exp\left[-(A_1+A_{123}+A_2)\right] I_0\left(\frac{v}{2}\right) I_0\left(\frac{v''}{2}\right) I_0(C_1) \times (G_0E_0'+\cdots+G_3E_3'); \tag{8}$$

where $v/2 = V_0/2RT$ and $v''/2 = V_0''/2RT$. The D_i and E_i are given in Eq. (12).[5] The E_i' are corresponding functions of (B_2+B_{123}). Finally,

$$\left.\begin{aligned}
G_0 &= I_0(C_2)I_0(C_{123}) \\
G_1 &= I_0(C_2)I_1(C_{123})D_{123}+I_1(C_2)I_0(C_{123})D_2 \\
G_2 &= I_0(C_2)I_0(C_{123})\left(\frac{D_2^2}{4}+\frac{D_{123}^2}{4}\right)+I_0(C_2)I_2(C_{123})\frac{D_{123}^2}{4}+I_1(C_2)I_1(C_{123})D_2D_{123}+I_2(C_2)I_0(C_{123})\frac{D_2^2}{4} \\
G_3 &= I_0(C_2)I_1(C_{123})\left(\frac{D_{123}D_2^2}{4}+\frac{D_{123}^3}{8}\right)+I_1(C_2)I_0(C_{123})\left(\frac{D_2^3}{8}+\frac{D_2D_{123}^2}{4}\right)
\end{aligned}\right\}. \tag{9}$$

In the summation method mentioned above we consider only the k configurations (over the rotational angles) in which V has its minimum value V_m. Suppose that $U^i = U_j^i$ and $U^a = U_j^a$ for the jth of these k positions. Then, replacing Eq. (6),[4] we have

$$K = K^0\frac{\sum_{j=1}^{k}\exp\left\{-\left[U_j^i+V_m\right]/RT\right\}}{\sum_{j=1}^{k}\exp\left\{-\left[U_j^a+V_m\right]/RT\right\}} \tag{10}$$

$$= K^0\frac{\sum_{j=1}^{k}\exp\left(-U_j^i/RT\right)}{\sum_{j=1}^{k}\exp\left(-U_j^a/RT\right)}. \tag{11}$$

In using Eq. (11) it is no longer necessary to employ approximate potential functions. That is, U_j may be calculated directly from the reciprocals of the intercharge distances in the jth configuration. However, in A_2 and A_{123} for glutamic acid, we still assume for simplicity a single

negative charge intermediate between the two oxygen atoms of a carboxylate group.

The procedure is essentially the same as before. The U_j^i and U_j^a are calculated from structural parameters with only the effective dielectric constant D_E unknown. Using experimental values of K and K^0, D_E is obtained by successive approximations.

Table IV compares effective dielectric constants calculated by the two methods: (1) integration, using approximate potential functions; and (2) summation over configurations for which V is a minimum. In general, the discrepancies between the D_E values calculated by the two methods increase with increasing charge separation. This is not surprising, however, for although the potential functions, used in the integrations, become more approximate with increasing intercharge distance, these functions are not employed in the summation method and therefore do not introduce a corresponding error in this case.

The effective dielectric constants given in column (4) of Table I have been calculated from Eq. (11), assuming a single D_E to hold for all configurations of both the acid and ion and for all interactions (in the case of A_{12} there are three charges and therefore three interactions; A_1, A_2, and A_{123} have, of course, only one interaction each). Thus, the values of D_E for K_1 (or K_{13}), K_2 (or K_{23}), and K_{132} (or K_{231}) are for simple interactions between charges which are in α, γ, and δ positions relative to each other, respectively. On the other hand, the effective dielectric constants for K_{12}, K_{21}, and K_{123} all involve A_{12} with three charges (and therefore α, γ, and δ interactions) and also either A_1 (α-interaction), A_2 (γ-interaction), or A_{123} (δ-interaction), respectively. It is therefore more difficult to attach definite physical significance to the D_E's calculated in these three cases. The question arises, in fact, in considering a molecule with more than two charges, such as A_{12}, as to whether it would not be more meaningful to assign different D_E's to the different interactions (e.g., α, γ, and δ in A_{12}), expecting them to be approximately the same as the corresponding D_E's calculated for the individual interactions. This procedure (the theoretical justification for which will be discussed in the fourth paper of the present series) would avoid the apparent contradictions which arise when the calculated D_E's apply to particular *equilibria* (each equilibrium involving two molecules) rather than to particular *molecules*. Thus, for example, in Table I there are three *different* D_E's each of which has been derived from a different equilibrium involving A_{12}. Which of these D_E's, if any, is to be used, say, in calculating the extent of electrostatic hindered rotation in A_{12} molecules?

TABLE IV. Effective dielectric constants D_E.

Substance	Integration, using approx. potential functions	Summation
α-charge effect		
Ethylene diamine	31.9 ($V_0=3400$)	31.0
Oxalic acid	33.9 ($V_0=1000$)	33.8
Glycine	39.4	39.4
Glutamic acid, K_1 (or K_{13})	36.3	36.3
β-charge effect		
1,3-Propane diamine	47.3 ($V_0=3400$)	44.1
β-Alanine	68.3	64.9
Malonic acid	30.1	29.9
γ-charge effect		
Glutamic acid, K_2 (or K_{23})	101. ($V_0=3400$)	82.6
δ-charge effect		
Glutamic acid, K_{132} (or K_{231})	*ca.* 160. ($V_0=3400$)	129.

The correct answer, as suggested above, is that the "effective" dielectric constant D_E should in general be considered different for each interaction between pairs of charges in a molecule, and for a given interaction we may expect D_E to approximate what it is found to be in an equilibrium in which only the single interaction is involved. Further, the data in Table I indicate that D_E for an interaction increases with increasing intercharge distance. In other words, ΔpK, for charge effects, falls off faster than can be accounted for by the increasing intercharge distance alone. The effective dielectric constant must also increase. This point will be discussed in Section II.

If the same D_E's for the individual interactions hold in both A_{12} and in A_1 (α), A_2 (γ), and A_{123} (δ), the charge effects should be additive. A comparison of columns (1) and (3) of Table I shows that they are nearly so for glutamic acid. Indeed, if, in evaluating the $\sum \exp(-U/RT)$, the first three D_E's in Table I are used for the α, γ, and δ interactions in A_{12} as well as in A_1, A_2,

TABLE V.

	(1) d	(2) ΔpK 25°C	(3) $2.00/d$	(4) D_E hindered rotation	(5) $1/(\overline{r^2})^{\frac{1}{2}}$	(6) $(4.75d+2.56)^{-\frac{1}{2}}$	(7) D_E free rotation	(8) $\frac{76d}{(1.86d+1)^{\frac{1}{2}}}$
Glycine	1	1.99	2.00	39.4	0.317	0.370	38.7	44.9
Glutamic acid (α)	1	2.15		36.3				
β-Alanine	2	1.06	1.00	64.9	.262	.288	60.0	70.0
Glutamic acid (γ)	3	0.80		82.6				
γ-Amino-butyric acid	3	0.72	0.67	92.0		.244		88.7
Succinic acid	3	0.69		88.0	.244		85.9	
Glutamic acid (δ)	4	0.44	0.50	129.		.215		103.
Glutaric acid	4	0.48		117.	.215		109.	
Adipic acid	5	0.39	0.40		.195	.195	122.	118.
Pimelic acid	6	0.34	0.33		.179	.179	128.	131.
Suberic acid	7	0.28	0.29		.167	.167	145.	142.
Azelaic acid	8	0.26	0.25		.157	.157	146.	153.

Dicarboxylic acid data are from R. Gane and C. K. Ingold, J. Chem. Soc., p. 2153 (1931).
Amino acid data are from reference 2.

and A_{123}, respectively, one calculates

$$\frac{\sum(12)}{\sum(1)}=10^{0.366}, \quad \frac{\sum(12)}{\sum(2)}=10^{1.718},$$

and

$$\frac{\sum(12)}{\sum(123)}=10^{2.958}, \tag{12}$$

where $\sum(12)=\sum \exp(-U_{12}/RT)$, etc. These values are (virtually) the same as those of column (3) in Table I, so that this calculation confirms the first sentence of the present paragraph.

Assuming that $D_E(\alpha)=36.3$, $D_E(\gamma)=82.6$, and $D_E(\delta)=129$ hold for A_1, A_2, and A_{123}, respectively, and that these D_E's are increased sufficiently in A_{12} to account for the observed lack of additivity of charge effects, a simple calculation shows that these values must become, in A_{12}, $D_E(\alpha)=36.8$, $D_E(\gamma)=83.7$, and $D_E(\delta)=131$ (if the three effective dielectric constants increase proportionally). Thus the discrepancy in additivity is accounted for by an increase in the effective dielectric constants of 1.3 percent.

Using $D_E=36.3$, 82.6, and 129 for the microscopic ions A_1, A_2, and A_{123}, respectively, and $D_E=36.8$, 83.7, and 131 for A_{12}, one may easily calculate the value of $|U_{\max}|-|U_{\min}|$ for each of these ions, where $U_{\max}$ and $U_{\min}$ are the maximum and minimum values of U over all angles. One finds -98 cal./mole for A_1 (as compared to -89 for glycine), -1560 cal./mole for A_2 (as compared to -746 for β-alanine), 1480 cal./mole for A_{123}, and -2500 cal./mole for A_{12}. As in previous cases, the electrostatic contribution to hindered rotation is apparently small compared to other contributions in A_2, A_{123}, and A_{12} (the corresponding value for these other contributions is approximately $2\times3400+1000=7800$), and it is trivial in A_1.

II. EFFECTIVE DIELECTRIC CONSTANTS

In this section we shall compare empirically the effective dielectric constants found for a number of substances with varying intercharge separation.

It has been pointed out elsewhere[3,5] that the ΔpK's for oxalic acid, malonic acid, ethylene diamine, and 1,3-propane diamine appear to be anomalous. We compare in Table V a number of other substances, particularly the normal dicarboxylic acids. Table V defines d (α, $d=1$; β, $d=2$; etc.) in column (1) and gives ΔpK (microscopic) in column (2). It is seen in column (3) that ΔpK can be represented approximately for these substances by $\Delta pK=2.00/d$. In column (4) are given the calculated values of D_E, assuming hindered rotation of the type discussed above. A number of these values have already been given. The remainder have been calculated using the same method (summation) and assumptions. In order to extend the data in an approximate manner, we shall also calculate D_E from the conventional

equation

$$\Delta pK = \frac{\epsilon^2}{kTD_E(\bar{r^2})^{\frac{1}{2}}}, \quad (13)$$

where $(\bar{r^2})^{\frac{1}{2}}$ is the root mean square intercharge distance, assuming free rotation and taking (except for glycine and β-alanine), as before, the negative charge of each carboxylate group as being midway between the oxygen atoms. The values of $1/(\bar{r^2})^{\frac{1}{2}}$ may be approximated by

$$\bar{r^2} = 4.75d + 2.56 \text{ (in } A^2\text{)}. \quad (14)$$

These calculations are shown in columns (5) and (6). The values of D_E in column (7) are calculated from columns (2) and (5), using Eq. (13). We may combine the two expressions $\Delta pK = 2.00/d$ and Eq. (14), and find, as an approximate empirical equation giving D_E as a function of d at 25°C,

$$D_E = 76d/(1.86d+1)^{\frac{1}{2}}. \quad (15)$$

This equation is used in obtaining column (8) of Table V.

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The Photolysis of Methylamine*

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The photolysis of methylamine has been shown to proceed essentially by two consecutive first-order reactions, the first to produce hydrogen, ammonia, and $CH_2 : NCH_3$; the second a dehydrogenation of the latter at a rate approximately double the first. A mechanism involving hydrogen atoms has been postulated. These have been shown experimentally to be present and also have been shown by discharge-tube experiments to react with methylamine.

THE reactions of atomic hydrogen and azomethane studied by Henkin and Taylor[1] yielded at 27°C only an addition compound, symmetrical dimethyl hydrazine. At 110°C, in addition to the hydrazine formation, methane and methylamine were obtained along with traces of ammonia. At 195°C the yield of methylamine increased but without a corresponding increase in methane or ammonia. It was concluded that methane production involved a rupture of the C−N bond in azomethane while methylamine production resulted from an N−N rupture in the hydrazine. The possibility also existed of a C−N rupture in methylamine. The photolysis of methylamine by Emeléus and Jolley[2] gave hydrogen and ammonia as the only gaseous products accompanying the molecule $CH_2 : NCH_3$, methyl methyleneimine. The photo-reaction is accompanied by a pressure increase. Since, however, the stable form of the imine is a trimer, a liquid of very low vapor pressure, the over-all reaction

$$2CH_3NH_2 = \tfrac{1}{3}(CH_2 : NCH_3)_3 + H_2 + NH_3$$

should not be accompanied by a pressure change. To resolve this difficulty and if possible, further elucidate the mechanism, the photolysis of methylamine was re-examined. This has also necessitated a study of the effect of hydrogen atoms introduced both by mercury sensitization and from a discharge tube.

EXPERIMENTAL

Photolysis Apparatus

The light source was a quartz spiral, low pressure mercury resonance arc operated at 5000 volt from a transformer carrying 6.3–6.4 amp. in the

* Abstract from a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, 1943.

[1] H. Henkin and H. A. Taylor, J. Chem. Phys. **8**, 1 (1940).

[2] H. J. Emeléus and L. J. Jolley, J. Chem. Soc., p. 1612 (1935).

TABLE I. Initial CH_3NH_2 200 mm. Temp. 100°C. Volumes in cc at N.T.P.

Time (min.)	Init. CH_3NH_2	NH_3 obs.	NH_3 calc.	Residual CH_3NH_2	H_2	H_2 formed CH_4	H_2 formed CH_3NH_2 dec.	x in C_2H_xN	ΔP (mm)
1.0	15.1	2.2	2.6	9.9	2.5	0.2	0.48	4.8	10.0
5.0	15.0	3.5	3.9	7.6	4.7	0.4	0.64	4.1	26.0
10.0	15.1	3.3	5.0	5.4	6.9	0.3	0.71	3.9	39.0
10.0	15.1	4.7	5.6	4.4	7.2	0.3	0.67	4.0	39.5
15.0	15.4	4.6	5.6	4.8	7.3	0.4	0.69	4.0	43.5
22.5	15.2	5.8	6.3	3.1	8.9	0.5	0.74	3.5	53.5
22.5	15.0	—	6.0	3.4	8.8	0.4	0.76	3.7	52.5
30.0	15.2	7.1	6.3	3.2	9.2	0.6	0.77	3.6	64.0
50.0	15.0	7.1	7.0	1.4	11.5	0.4	0.85	3.4	72.5
70.0	14.9	7.5	7.4	0.6	12.2	0.5	0.85	3.3	81.5
90.0	14.9	—	7.7	0.0	12.4	0.6	0.83	3.3	82.5

primary. The spiral surrounded the quartz reaction vessel, 2.5 cm in diameter, 11.5 cm in length, and 57.0 cc in volume. In the early experiments the reaction vessel and lamp were submerged in a water bath at 75°C. In later experiments this was replaced by a steam jacket. The necessity for constant temperature so far as the lamp is concerned is the necessity for constant intensity of the light. Some difficulty was experienced in achieving this, since, if the lamp before striking the arc was at 100°C, the temperature would rise upon striking the arc. Despite adjustment based on preliminary trials, the results show evidence of a high reaction rate during the first minute or so. A correction, however, can be applied for this as is shown later.

The methylamine was prepared from the hydrochloride by treatment with moist potassium hydroxide in vacuum and dried over barium oxide. Hydrogen and propylene used in several runs were taken from tanks. Hydrogen was purified by passage over hot platinized asbestos followed by drierite. Propylene was not further purified.

For a run, methylamine was introduced at the desired pressure into the reaction vessel which was already heated. The lamp was turned on and pressure readings taken at chosen time intervals. At the conclusion of the experiment the products were drawn through a trap in liquid nitrogen by means of a Toepler pump. The uncondensed gases were analyzed in a Fisher gas analyzer. The material condensed in the liquid nitrogen trap was subjected to a distillation from −119°, using melting ethyl bromide, to liquid nitrogen temperature to separate ammonia from methylamine. Finally the fraction volatile at dry ice temperature was drawn off and measured as methylamine.

Hydrogen Discharge Apparatus

A Wood's discharge tube of the conventional type was used as the source of hydrogen atoms. The tube, 10-mm inside diameter, was water cooled over its length of 50 cm between the electrodes, which were of sheet aluminum, 1.5 mm thick bent into cylinders 23 cm long and 3 cm in diameter. A 2-kva transformer operated on 220 volts in the primary furnished the excitation for the discharge. Hydrogen was introduced near each electrode and removed at the center of the discharge. It passed thence about 30 cm to the reaction vessel of 500-cc volume, entering through a constricted nozzle to impede back diffusion into the arc. Concentrated sulfuric acid was used as a poisoning agent to prevent atom recombination on the walls. The flow system for the atom experiments used hydrogen at 0.5–0.8-mm pressure as read on a McLeod gauge and methylamine drawn from a reservoir at −78°C, where the vapor pressure is 7–8 mm, through a capillary flow meter under a pressure difference of 5–7 mm as read on a sloping manometer. The partial pressure of methylamine in the reaction vessel was always less than that of the hydrogen. In all runs the reaction vessel was maintained at 100°C.

EXPERIMENTAL RESULTS

Methylamine

Table I contains a summary of the information obtained from the study of the photolysis of methylamine. The pressure change is that observed when the contents of the reaction vessel were again at room temperature after completion of the run. The initial pressure under similar conditions was ~200 mm in all runs. Hydrogen and methane were determined by combustion in oxygen to water and carbon dioxide. No nitrogen was found in any of the work. Ammonia, identified using Nessler's reagent, was separated from undecomposed methylamine as already described. Experiment with known mixtures of methylamine and ammonia showed that the method is not too satisfactory in that methylamine has a small vapor pressure even

at −119°C. A 10–15-min. distillation was found to be reasonably reliable.

Since no nitrogen was found and since hydrogen, ammonia, and methane were the only gaseous products, it is probable that the carbon to nitrogen ratio in the residual products must be 2 : 1. If we assume this, the ammonia and methylamine volumes can be calculated from the total volume of the mixture. Thus since each contains one nitrogen, knowledge of the initial methylamine and the final methylamine plus ammonia gives the residual nitrogen in the residue. Twice this is then the carbon in the residue. This latter plus the carbon in the methane corresponds to the methylamine decomposed. The difference between the undecomposed methylamine and the total ammonia plus methylamine gives the ammonia. Comparison between ammonia values calculated in this way and those obtained by the distillation method show good agreement and whereas the distillation values for the ammonia produced as a function of the time of photolysis are somewhat scattered, the values calculated by the above method lie on a smooth curve that averages the scattered experimental values. The assumption is therefore justified. After some ten such runs with distillation separation of the products, the total volume of ammonia and methylamine alone was measured and the individual volumes obtained by the calculation. A brownish deposit which appeared to be liquid was always observed in the reaction vessel after the longer runs.

In all the experiments reported in Table I the reaction vessel was separated from the rest of the system by plugs of gold foil and gold sponge in the inlet tubing.

Methylamine and Mercury

Since the lamp used as a source of radiation was a resonance lamp and since considerable quantities of hydrogen are produced in the methylamine photolysis, the effect of mercury vapor on the rate of the reaction was studied. Table II summarizes the results obtained. For run number 25 methylamine was passed through plugs of gold foil and gold sponge in the lines connecting the reaction vessel with the mercury manometer. For run number 23 the gold was not present and the system was saturated with mercury vapor at room temperature. For number 24 several drops of mercury were present in the reaction vessel which in all these runs was at 75°C. It will be observed that the rate of pressure increase is in no way altered by the presence of mercury in the reaction vessel. This might be interpreted that hydrogen atoms have no part in the reaction. To test for the presence of hydrogen atoms during the methylamine photolysis the following runs were made in presence of propylene.[3]

TABLE II. Effect of mercury at 75°C.

Run	Hg press. mm	CH_3NH_2 P_0 in mm	ΔP in mm 1 min.	3 min.	5 min.	10 min.	15 min.	20 min.	30 min.
25	0	101.5	9.5	20.5	27.5	37.5	—	46.0	47.5
23	$\sim 2\times10^{-3}$	100.0	9.5	22.5	29.0	39.0	43.0	44.0	45.0
24	$\sim 7\times10^{-2}$	100.0	8.0	19.5	27.0	37.0	42.5	45.5	47.5

TABLE III. Effect of propylene at 75°C.

CH_3NH_2 cc	C_3H_6 cc	ΔP in mm 1 min.	3 min.	5 min.	10 min.	cc C_3H_8 after 60 min.	cc C_6H_{14} after 60 min.
7.5	0.0	8.0	19.5	27.0	37.0	0.0	0.0
0.0	23.8	4.5	− 1.5	− 7.5	−21.5	0.9	2.6
7.5	22.9	−3.0	−18.5	−33.5	−59.5	2.3	1.6
ΔP calc.		7.5	17.0	26.0	38.0		

Methylamine and Propylene

Table III shows the data obtained in some typical runs. The volume of propane was determined by slow combustion of the gas pulled off dry ice after removal of methylamine, ammonia, and residual propylene. The volume of the hexanes was estimated from the pressure exerted by the residue from dry ice when vaporized in a known volume.

Since propylene polymerizes in the radiation used, a pressure decrease is observed. With methylamine and propylene a larger pressure decrease is found and the difference is seen in the table to be entirely comparable with the pressure increase found with methylamine alone. The volumes of the hydrocarbons obtained after sixty minutes of irradiation show a marked increase in propane and decrease in hexane when methylamine is present. It must be concluded

[3] C. H. Bamford, J. Chem. Soc., p. 17 (1939).

that hydrogen atoms are present during methylamine photolysis and also that the excess of propylene has no great effect on the rate of the photolysis.

Methylamine and Hydrogen

To test the effect of the hydrogen produced during the photolysis on the course of the reaction several runs were made in which hydrogen was added to the methylamine before irradiation commenced. Table IV gives these data in a manner similar to that in Table I.

It will be seen that the general course of the reaction is identical with that in the absence of added hydrogen both from the point of view of the amount of methylamine decomposed, from the rate of pressure change, as also from the formula of the residual product.

Methylamine and Hydrogen Atoms

Since the experiments with propylene show that hydrogen atoms are present and, furthermore, that the general course of the reaction is unaffected, it is necessary to test specifically for the effect of hydrogen atoms on methylamine. To this end hydrogen atoms from a Wood's discharge tube were led into a stream of methylamine at 100°C as already described. No attempt was made to measure the atom concentration though preliminary experiments with chlorine showed a relatively high concentration must be present. The extent of reaction of the hydrogen atoms with methylamine was measured by the amount of ammonia produced as given by the distillation separation from methylamine. In view of the poor reliability of the separation a direct comparison was made between two runs in which the arc was operating and two runs, otherwise identical, but without the arc. The distillation separation was performed on the products collected in liquid nitrogen in each run, to give what is termed "apparent" ammonia but what in the absence of the arc must be methylamine. Table V gives the comparative data and leaves no doubt that ammonia is produced in considerable quantity from hydrogen atoms and methylamine at 100°C. It should also be mentioned here that examination of the gases not condensed by liquid nitrogen showed unreacted hydrogen and small amounts of methane comparable in terms of the methylamine decomposed with those found in the photolysis. No nitrogen was observed.

TABLE IV. Effect of hydrogen. Temp. 100°C. Volumes in cc at N.T.P.

Time (min.)	Init. CH_3NH_2	Init. H_2	Residual CH_3NH_2	NH_3 calc.	H_2 obs.	CH_4 obs.	x in C_2H_xN	ΔP (min.)
5.0	15.0	16.7	6.8	4.2	22.7	0.2	3.9	26.0
10.0	15.2	15.2	5.2	5.1	22.7	0.2	3.9	39.0
22.5	14.9	16.2	3.1	6.1	25.9	0.4	3.5	51.5
50.0	15.0	15.6	1.8	6.7	27.1	0.2	3.4	63.0
90.0	14.9	15.8	0.3	7.4	29.0	0.2	3.3	73.5

TABLE V. Effect of hydrogen atoms. Temp. 100°C.

		Time of distillation							
		10 min.				15 min.	20 min.		
Run number →		1	*2A	2B	Av. %	1	1	2	Av. %
Arc on	CH_3NH_2	1.1	0.9	1.1		0.7	1.0	0.4	
	NH_3	2.4	3.2	3.0		2.8	2.5	3.7	
	Apparent % NH_3	69	78	73	73	78	72	90	81
Arc off	CH_3NH_2	5.5	3.5	3.5		4.6	2.5		
	NH_3	0.6	0.7	0.7		1.5	1.7		
	Apparent % NH_3	10	17	17	15	25	40		40

*2A and 2B are duplicate distillations on the same sample after refreezing in liquid nitrogen.

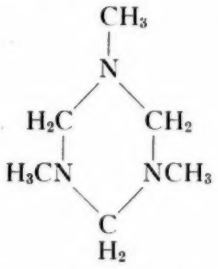
$C_6H_{15}N_3$ Photolysis

For reasons which will appear in the discussion the trimer of methylmethyleneimine, that is, trimethyltrimethylene triamine, was prepared and subjected to photolysis. The preparation employed the method given by Henry[4] of treating aqueous methylamine with aqueous formaldehyde at 0°C. The triamine is salted out with potassium hydroxide as a light oily layer which is dissolved in absolute ether and dried with potassium hydroxide pellets. After removing the ether on a steam bath, distillation at 22 mm gave the product at 64–65°C in good agreement with the value reported in Beilstein 68.3°C at 26 mm. A picrate of the product, without recrystallization, melted at 119–122°C; the value reported by Duden and Scharff[5] is 127–128°C. The refractive index to the sodium D lines was 1.4600 at 19°C; Beilstein reports 1.4632.

[4] L. Henry, Bull. Acad. Roy. Belg. **26**, 200 (1893); **28**, 359, 360 (1895); **29**, 26 (1896).

[5] P. Duden and M. Scharff, Ann. d. Chemie **288**, 251 (1895).

Travers and co-workers[6] studying the thermal decomposition of the methylamines report the presence of methylmethyleneimine monomer in the gas phase. To investigate the possible depolymerization of the trimer a vapor pressure-temperature study was made. The data are given in Table VI. A plot of the logarithm of the vapor pressure against the reciprocal temperature is not perfectly straight but shows a small decrease in slope with increase in temperature. The slope of the best straight line corresponds to a molar heat of vaporization of 11,750 cal. Application of Trouton's rule gives a value of 9600 cal. Now a calculation of the molecular refraction for the trimer from atomic refraction equivalents, assuming the structure to be



is 39.5. The refractive index value found, when used in the Lorenz-Lorentz relation, gives a molecular refraction of 38.4. This agreement shows that the liquid is essentially trimer. The relatively high value of the heat of vaporization and its excess over the Trouton figure would seem to indicate some dissociation to the monomer with increase in temperature.

Because of the low vapor pressure of the trimer the photolysis was carried out in a liter quartz reaction vessel at room temperature. The data are presented in Table VII. The formula of the residue is calculated from a carbon, hydrogen, and nitrogen balance and then expressed with one atom of nitrogen. The 0.5-cc ammonia in the first run did not give a good test with Nessler's reagent and may have been contaminated with the residue from the run. Since in the second run, for 15.75 hr., methane production appears to have increased at the expense of the hydrogen, a third run with hydrogen present initially was made. Here, however, the results again parallel those in the absence of added hydrogen and the high methane in the second run must be considered unreliable.

TABLE VI.

Vap. press. mm	Temp. °C
4.0	26.0
32.0	58.0
33.0	58.5
150	89.5
154	90.0
344	114.0
349	115.0
351	117.0

[6] A. G. Carter, P. A. Bosanquet, C. G. Silcocks, M. W. Travers, and A. F. Wilshire, J. Chem. Soc., p. 495 (1939).

TABLE VII. $C_6H_{15}N_3$ photolysis. Temp. 28°C.

Time hr.	$C_6H_{15}N_3$ cc init.	H_2 cc init.	NH_3 cc obs.	H_2 cc obs.	CH_4 cc obs.	Residue formula
4.00	3.5	—	0.5(?)	2.0	0.5	$C_{2.2}H_{3.3}N_{1.0}$
15.75	6.3	—	1.0	1.9	1.8(?)	$C_{2.0}H_{3.3}N_{1.0}$
4.00	3.5	11.2	0.2	12.8	0.8	$C_{1.9}H_{3.2}N_{1.0}$

DISCUSSION

Inspection of the results in Table I shows that hydrogen production increases steadily per unit of methylamine decomposed. Initially two methylamines give one hydrogen but towards the completion of the decomposition the results approach one hydrogen for one methylamine. The ratio of ammonia produced to methylamine decomposed, on the other hand, remains constant throughout the decomposition at 0.5. Such results may be interpreted by a primary decomposition of methylamine to give hydrogen, ammonia, and a residue which undergoes further dehydrogenation. Emeléus and Jolley have suggested as the over-all reaction:

$$2CH_3NH_2 \rightarrow H_2 + NH_3 + CH_2 : NCH_3.$$

The probable existence of the methylmethyleneimine was shown when a Schryver's test for formalydehyde was obtained in an aqueous solution of the non-volatile liquid from a run and also by forming a phenylhydrazone. In the present work positive formaldehyde tests were obtained with Schiff's reagent. The test was found to be less pronounced, however, with the longer runs. In one experiment after irradiation for twelve hours, a weak positive test with Schiff's

reagent only appeared after 20–30 minutes standing. This might be attributed either to a smaller amount of the residue or more probably to a slower hydrolysis of the residue to formaldehyde. Finally, the calculated formula of the residue as shown in Table I appears for short runs to approximate C_2H_5N but for long exposures to approach C_2H_3N.

Travers and co-workers in the pyrolysis of the three methylamines report that the formula of the non-volatile residue from both di- and tri-methylamine approximated C_2H_5N but that for longer runs the hydrogen content was lower. Using data reported in their paper for the two longest runs the residues may be calculated to be $C_{2.0}H_{4.2}N_{1.0}$ and $C_{2.0}H_{4.1}N_{1.1}$. It seems probable that had the length of the run been further increased the residues would have approached C_2H_3N as found here.

The increased production of hydrogen over that of ammonia was observed by Emeléus and Jolley but no explanation was offered for it. If the above equation were to represent the true over-all reaction, then, since the stable form of the imine is the trimer, a saturated triamine, a stable liquid of low vapor pressure, no pressure change should occur. Actually a marked pressure change is observable even in the shortest runs and seems to approach, though falling somewhat short of a fifty percent pressure increase on completion. It is apparent that the over-all reaction should better be represented as

$$2CH_3NH_2 \rightarrow 2H_2 + NH_3 + C_2H_3N.$$

Table VI actually shows that the vapor pressure of the trimer is far too high at the temperature of the experiments to account for the observed pressure change. It is not now possible to say what C_2H_3N represents. It is probable that it is a polymer of $CH_3N : C$ or CH_3CN. Many such polymers are known but all contain carbon-carbon bonds and none even vaguely resembles the triamine $C_6H_{15}N_3$. This would suggest that even if the triamine is formed it is probably the monomer $CH_2 : NCH_3$ that dehydrogenates to the isonitrile which subsequently polymerizes.

The results from the photolysis of the triamine show that a dehydrogenation can occur under the experimental conditions. However, in order to obtain comparable amounts of decomposition as with methylamine very long exposures were necessary which again indicate that it is the monomer which reacts rather than the trimer. One further point is significant from the triamine photolysis, namely, that traces of ammonia and methane were also found. It would seem, then, that the source of the traces of methane found in the methylamine photolysis is the imine rather than from an alternative carbon-nitrogen rupture of the methylamine molecule.

The photolysis in presence of mercury vapor shows that hydrogen atoms have no appreciable effect on either the products of reaction or on the rate of the decomposition. That hydrogen atoms are present during the photolysis even in the absence of mercury vapor is seen from the results with propylene. It must be concluded, therefore, that reactions both producing and consuming hydrogen atoms are present and an internal balance of these is maintained despite additional reactions which would produce or would consume these atoms. One such hydrogen atom consuming reaction, namely, that with methylamine itself has been tested and shown to occur readily at 100°C to yield ammonia in considerable amounts and traces of methane.

These facts are consistent with the following mechanism:

$$CH_3NH_2 \xrightarrow{h\nu} CH_3NH + H, \quad (1)$$

$$CH_3NH + H \rightarrow CH_3NH_2, \quad (2)$$

$$CH_3NH \rightarrow CH_2 : NH + H, \quad (3)$$

$$CH_2 : NH + CH_3NH_2 \rightarrow CH_2 : NCH_3 + NH_3, \quad (4)$$

$$CH_3NH_2 + H \rightarrow CH_3NH + H_2, \quad (5)$$

$$CH_2 : NCH_3 \rightarrow C_2H_3N + H_2. \quad (6)$$

Reaction (1) seems to accord best with the absorption data on ammonia and the amines as an excitation of an electron localized in the amine group. It is consistent with the results for other amines[3] as also for dimethyl hydrazine.[7] Emeléus and Jolley express the fate of the methylamino radical, CH_3NH, by the reaction:

$$2CH_3NH \rightarrow CH_2 : NCH_3 + NH_3.$$

[7] W. L. Kay and H. A. Taylor, J. Chem. Phys. 10, 497 (1942).

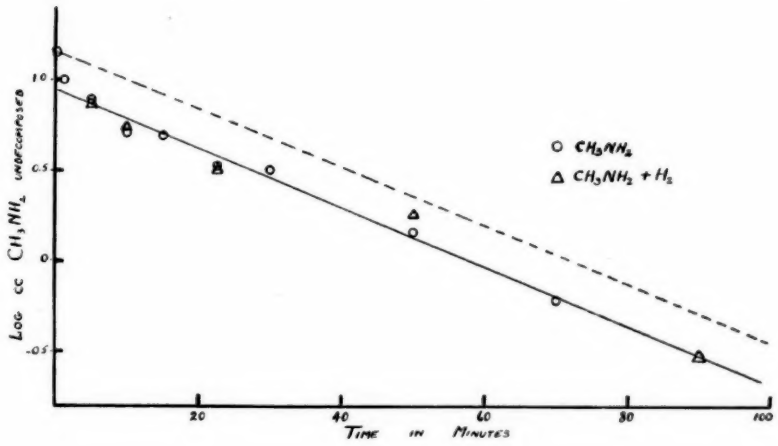


FIG. 1.

Such a reaction between two radicals must be of rare occurrence unless the equation is merely to be taken as an over-all reaction. It appears plausible to offer a mechanism for the production of the imine through reactions (3) and (4). Reaction (3) as a unimolecular decomposition of a radical could conceivably be quite slow. Methyleneimine $CH_2 : NH$, on the other hand, should be as relatively stable as ketene. Its postulation permits a parallelism to be drawn between methylamine photolysis and pyrolysis in that in the latter the high temperature could cause decomposition of the methyleneimine to hydrogen and hydrogen cyanide, which are found, before it could react with methylamine to produce ammonia which is found only in small amounts in the thermal decomposition.

Reaction (5) between hydrogen atoms and methylamine leading to the methylamino radical and hydrogen accounts for the similarity of the results found here from the photolysis and from the discharge-tube experiments. Reactions (3) and (5), however, form a chain series and hence a large quantum yield would be expected for the over-all reaction. Emeléus and Jolley have estimated the quantum yield from a comparison between methylamine and ammonia decompositions and although the reported value ~0.7 cannot be considered exact, it seems nevertheless certain that no long chains can be present. Reaction (2), the reverse of (1), will account for the low quantum yield and a simple calculation will show that a difference between the energies of activation of reactions (2) and (3) of 10–15 kcal. would give a quantum yield of unity. Such a value is at least plausible.

Reaction (6) is intended as an over-all reaction rather than one describing a mechanism. It does not seem possible from the following analysis, however, that it could involve hydrogen atoms and it may very well be a simple dehydrogenation.

Evaluation of the stationary concentrations of hydrogen atoms and methylamino radicals, assuming, in view of the observed rapid ammonia production, that reaction (4) follows rapidly on (3), that is, that methyleneimine does not build up appreciably in the system, gives

$$[CH_3NH]=(k_1k_5/k_2k_3)^{\frac{1}{2}}[CH_3NH_2]$$

and

$$[H]=(k_1k_3/k_2k_5)^{\frac{1}{2}}.$$

The rate of the over-all reaction is then given by:

$$-d[CH_3NH_2]/dt=2(k_1k_3k_5/k_2)^{\frac{1}{2}}[CH_3NH_2],$$

which is also twice the rate of production of ammonia. These, then, should be of first order in terms of methylamine. The data in Tables I and IV are plotted in Fig. 1 as the logarithms of undecomposed methylamine against time. The plot is linear in agreement with the first-order requirement and the slope of the line gives a value for the velocity constant of 0.036 min.$^{-1}$. It will be noted, however, that the line does not pass through the point corresponding to the initial concentration nor to the data from the

TABLE VIII. Calculated pressure change.

Corr. time min.	ΔP obs. mm	ΔP calc. mm
10	10	9.5
20	26	27.0
30	43.5	44.5
35	53	53.0
40	—	59.0
45	64	64.0
50	—	70.5
60	—	79.0
65	72.5	82.5
80	82	89.5

one-minute run. This has been attributed to a temporary high initial intensity in the lamp. If the dotted line in Fig. 1 be drawn parallel to the "observed" line but passing through the zero time value it is possible to correct the observed times of reaction to discover what times would have been required had the lamp intensity remained constant. This is tantamount to a calculation of the velocity constant from point to point during the course of the reaction when a steady state in the lamp had been achieved and an interpolation for the early stages. The correction amounts to about 10–15 min.

It is now possible to treat the observed pressure changes at these corrected times as due to two consecutive first-order reactions:

$$2CH_3NH_2 \xrightarrow{k_A} H_2 + NH_3 + CH_2 : NCH_3,$$

$$CH_2 : NCH_3 \xrightarrow{k_B} H_2 + C_2H_3N,$$

on the assumption that the net pressure change measures the C_2H_3N production. The rate of disappearance of methylamine, 0.036 min.$^{-1}$, measures k_A. Hence k_B may be calculated. The value is found to be 0.075 min.$^{-1}$. Using these velocity constants the pressure changes for 200-mm methylamine may be calculated and are compared with the observed values after various times in Table VIII. The agreement during the first 45 min. which corresponds to about 80 percent reaction is excellent. The low observed values, as compared with those calculated, later in the reaction are to be associated with an alternative loss of the methyl methyleneimine other than that accounted for in the above scheme, for example, as the polymer, the triamine, or in the methane-producing reaction. In any event, it is apparent that the rate of pressure change is a reliable measure of the rate of reaction and hence that the conclusions drawn earlier that the presence of mercury, of hydrogen, and of propylene has little if any effect on the rate of reaction is justified. It is possible, of course, that in all these cases the change in the hydrogen atom concentration was too small to have a noticeable effect. From the experiments with hydrogen atoms it would seem this must be the case. Thus approximately 2.5 cc ammonia were produced from 7 cc of methylamine during a discharge-tube run. These 7 cc passed through the system in 60 min. At a pressure of 0.2 mm this would be 440 cc per min. The hydrogen rate was 1520 cc per min. at 0.6-mm pressure. This total rate of flow, 1960 cc per min., for a reaction vessel of 500-cc capacity means a contact time of ~0.25 min. From the rate constant of the photolysis, 0.036 min.$^{-1}$, the amount of methylamine decomposed in 0.25 min. from an initial 7 cc would be only 0.06 cc or half this amount of ammonia produced. The discharge-tube rate is thus some eighty times larger due undoubtedly to the relatively high atom concentration. It must be emphasized, however, that this increased ammonia production in the discharge-tube experiments is not accompanied by a corresponding increase in alkane production. It is therefore unlikely that methyl radicals are present. Hence reaction (5) probably represents the initial step under these conditions.

On the basis of the proposed mechanism the low quantum yield is to be traced essentially to the slowness of reaction (3), the decomposition of the CH_3NH radical. This would probably mean a fairly high activation energy for this reaction, which in turn should be reflected in an over-all activation energy for the photolysis. The sensitivity to temperature early in the runs reported may be due in part to this source as well as to variation in lamp intensity. It is proposed to measure the quantum yield more accurately and also the effect of temperature over-all in order to test these points.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Hyperconjugation in Paraffin Hydrocarbons

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IT has been found empirically that the heats of combustion of the normal paraffin hydrocarbons form a very nearly linear function of the number of carbon atoms per molecule.[1] This fact seems reasonable, since it is easily shown to be a consequence merely of the approximate constancy of the bond energies. Small deviations from linearity do occur, however, with the lower members of the series, and especially with methane.

With the discovery that hyperconjugation[2] is apparently a significant feature of the structures of even saturated hydrocarbons, two questions arise. Would the resonance energies, which result from the hyperconjugation, be expected to affect significantly the approximate linearity of the heats of combustion, and can they be used to account for the observed deviations from linearity? The calculations reported below suggest that the answer to both questions is "No."

The method of calculation is that of Mulliken and coworkers, and the symbols used below have the meanings assigned by them.[2,3] In order that the calculations can be carried through at all, the paraffin molecules must be assumed to have extended zig-zag configurations, in which all the carbon atoms of each lie in the same plane. Such configurations seem to obtain in the crystals of the solid paraffins and probably represent the most stable arrangements of the atoms. If this assumption is made, and if the non-orthogonality integrals S are neglected, the general solution of the secular equation is[4]

$$E_j=\alpha+\left[\cos\frac{\pi j}{n+1}\pm\left(\cos^2\frac{\pi j}{n+1}+\eta^2\right)^{\frac{1}{2}}\right]\gamma, \qquad (1)$$

where E_j is the energy of the jth molecular orbital that is antisymmetric with respect to the plane of the carbon atoms; j is a parameter that is allowed to assume the values 1, 2, ... n; n is the number of carbon atoms in the molecule; and α, η, and γ have their conventional meanings.[2,3] If the integrals S are not to be neglected, the "corrected" energies of the orbitals can be calculated by the method of Wheland[5] with the use of the E_j's of Eq. (1).

When the sums of the energies of the occupied orbitals are computed from Eq. (1), the resulting values are found to be almost exactly linear in n, regardless of the assumed value of η, and whether the integrals S are neglected or not. Consequently, the resonance energy due to the hyperconjugation can be considered merely to increase the energy of each carbon-carbon single bond without appreciably affecting its constancy from substance to substance. The very small deviations from linearity that are calculated are actually in the wrong direction to account for the observed, much larger deviations in the heats of combustion.

The conclusion to be derived from the above discussion is that the "second-order hyperconjugation" which has been considered can be ignored in discussions of molecular energies, since it does not affect appreciably the rule of constancy of bond energies. The exceptions to this rule which are observed must therefore presumably be due to other causes.

[1] F. D. Rossini, Bur. Stand. J. Research **6**, 39 (1931); **12**, 735 (1934); **13**, 21 (1934).
[2] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).
[3] R. S. Mulliken and C. A. Rieke, J. Am. Chem. Soc. **63**, 1770 (1941).
[4] This general solution was obtained by standard methods. For a discussion of the solution of a similar equation, see P. S. Epstein, Phys. Rev. **41**, 91 (1932).
[5] G. W. Wheland, J. Am. Chem. Soc. **63**, 2025 (1941).